PAT-NO: JP02000223153A

DOCUMENT-IDENTIFIER: JP 2000223153 A

TITLE: LITHIUM ION SECONDARY BATTERY

PUBN-DATE: August 11, 2000

INVENTOR-INFORMATION:

NAME	COUNTRY
SHIGA, TORU	N/A
AOKI, YOSHIFUMI	N/A

ASSIGNEE-INFORMATION:

NAME	COUNTRY
TOYOTA CENTRAL RES & DEV LAB INC	N/A

APPL-NO: JP11021522

APPL-DATE: January 29, 1999

INT-CL (IPC): H01M010/40, H01M004/04 , H01M004/58

ABSTRACT:

PROBLEM TO BE SOLVED: To provide a secondary battery indicating a good discharge characteristic when lithium manganese oxide having a spinel structure is used for a positive electrode, by containing a specific amount of malonic diester in organic electrolyte.

SOLUTION: Organic **electrolyte** contains 0.5-3.0 vol% of malonic diester. Preferably, the malonic diester is **diethyl malonate** or di-n-propyl malonate. Since the organic **electrolyte** contains the malonic diester, a cycle characteristic is greatly improved. The malonic diester decomposes on a negative electrode surface during charge, good coating for accelerating going in/out of lithium ions is formed. As solvent of 97-99.5% other than the malonic diester, for example, cyclic carbonate class such as ethylene carbonate, chain carbonate class such as dimethyl carbonate or diethyl carbonate, lactone class such as γ- buthrolactone, or composite solvent such as sulfolane is used.

DERWENT-ACC-NO: 2000-631061

DERWENT-WEEK: 200061

TITLE: Lithium ion secondary battery comprises cathode, anode containing spinel structured lithium manganese oxide and organic electrolyte containing predetermined amount of containing malonic acid diester

PATENT-ASSIGNEE: TOYOTA CHUO KENKYUSHO KK[TOYW]

PRIORITY-DATA: 1999JP-0021522 (January 29, 1999)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 2000223153 A	August 11, 2000	N/A	006	H01M 010/40

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP2000223153A	N/A	1999JP-0021522	January 29, 1999

INT-CL (IPC): H01M004/04, H01M004/58 , H01M010/40

ABSTRACTED-PUB-NO: JP2000223153A

BASIC-ABSTRACT:

NOVELTY - The lithium ion secondary battery consists of cathode containing carbon, anode containing spinel structured lithium manganese oxide and organic **electrolyte** containing 0.5-3 vol % of malonic acid diester. The malonic acid diester is preferably **diethyl malonate** or malonic acid di n-propyl.

USE - For power supply.

ADVANTAGE - The battery has excellent charging and discharging property.

CHOSEN-DRAWING: Dwg.1/1

TITLE-TERMS: LITHIUM ION SECONDARY BATTERY COMPRISE CATHODE ANODE CONTAIN
SPINEL STRUCTURE LITHIUM MANGANESE OXIDE ORGANIC ELECTROLYTIC CONTAIN PREDETERMINED AMOUNT CONTAIN MALONIC ACID

DERWENT-CLASS: E19 L03 X16

CPI-CODES: E10-G02G2; E35-S; L03-E01B8; L03-E01C;

EPI-CODES: X16-B01F1; X16-E01C1; X16-J02; X16-J08;

CHEMICAL-CODES:
Chemical Indexing M3 *01*
Fragmentation Code
J0 J012 J2 J272 M210 M213 M231 M272 M282 M311
M321 M342 M382 M391 M416 M620 M782 M904 M905 Q454
R023
Specfic Compounds
A2N5GK A2N5GM

Chemical Indexing M3 *02*
Fragmentation Code
J0 J012 J2 J272 M210 M212 M272 M282 M311 M321
M342 M382 M391 M416 M620 M782 M904 M905 M910 Q454
R023
Specfic Compounds
00774K 00774M
Registry Numbers
0774U

Chemical Indexing M3 *03*
Fragmentation Code
A103 A313 A425 A940 A980 C108 C550 C730 C801 C802
C803 C804 C805 C807 M411 M782 M904 M905 Q454 R036
Markush Compounds
200026-36501-K 200026-36501-M

UNLINKED-DERWENT-REGISTRY-NUMBERS: 0774U

SECONDARY-ACC-NO:
CPI Secondary Accession Numbers: C2000-189627
Non-CPI Secondary Accession Numbers: N2000-467733

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to a rechargeable lithium-ion battery and the rechargeable lithium-ion battery which improved the organic electrolytic solution and raised the charge-and-discharge cycle especially.
[0002]
[Description of the Prior Art] In recent years, the spread of electric vehicles is cried for from environmental problems, such as air pollution. In connection with this, high performance-ization of the cell which is the power source is called for. The negative electrode which consists of a positive electrode which consists of a lithium transition-metals multiple oxide, and a carbon material conventionally, and the rechargeable lithium-ion battery which consists of the organic electrolytic solutions are known as 1 of a high performance cell, and there is the description that energy density is high.

[0003] The rechargeable lithium-ion battery is already put in practical use by the portable electronic device etc. However, layer-like lithium cobalt oxide is used for this conventional lithium secondary battery as a positive electrode, and it has the problem that the cost of the cobalt which constitutes this is high and is a few resource.
[0004] On the other hand, in the electric vehicle, it is cheap, and since it is important to constitute a cell using the abundant matter of a resource, instead of layer-like lithium cobalt oxide, the lithium manganic acid ghost of Spinel structure attracts attention. However, compared with the rechargeable lithium-ion battery of lithium cobalt oxide, it is known for the rechargeable lithium-ion battery which used the lithium manganic acid ghost for the positive electrode that cell capacity will fall remarkably with the repeat of charge and discharge, and amelioration of the charge-and-discharge SAIKU property is indispensable.
[0005]
[Problem(s) to be Solved] Now, when the negative electrode in the condition that the lithium ion was charged, and the solvent in the electrolytic solution react, it is mentioned to one of the causes of a fall of the cell capacity accompanying a charge-and-discharge cycle that a part of lithium ion which can discharge deactivates. Moreover, since the lithium ion which deactivated serves as a coat of a lithium compound with big electric resistance and exists in the front face of a negative-electrode active material, it bars receipts and payments of other lithium ions.
[0006] The electrolytic-solution solvent used widely now is the multicomputer system of the annular carbonate of a high dielectric constant centering on ethylene carbonate, and the chain-like carbonate of low viscosity, such as diethyl carbonate and dimethyl carbonate. However, also in these electrolytic-solution systems, it reacts gradually with the negative electrode of a charge condition. Then, many things for which another solvent is used are proposed. For example, it argues about the possibility of comparatively cheap ester solvent, such as methyl acetate and ethyl acetate.
[0007] However, ester solvent is lacking in reducibility-proof, and tends to react with the negative electrode which carried out occlusion of the lithium ion. Then, it mixes with a carbonate system solvent and is used in many cases. For example, ethyl acetate is mixed with a carbonate system solvent by the volume ratio 1:1 or 3:2, and the cell which uses a LiCo02/natural graphite as an electrode is proposed (JP,4-249071,A). Moreover, invention which raises the safety of the cell which adds methyl butyrate and butyl acetate 0.5 to 3.0%, and uses a LiCo02/carbon material as an electrode is proposed (JP,7-320777,A).
[0008] Moreover, the example of the cell by which the proposal that a battery life became long was made when the benzoate used for JP,10-255836,A the electrolytic solution which occupies 1 - 40% of a solvent, and the lithium cobalt oxide was used for the positive electrode, and it used the natural graphite for the negative electrode is shown. However, it is not illustrated [each] whether the lithium manganic acid ghost of Spinel structure is applicable to the cell used as a positive electrode.

[0009] On the other hand, the cell which consists of a lithium metal and a carbon material is proposed as a case where ester solvent is used independently, by using as a solvent the diethyl malonate which has two ester bonds in intramolecular (JP,8-190932,A). However, when it applied to the rechargeable lithium-ion battery which consists of a lithium manganic acid ghost and a carbon material so that it might mention later, it became clear that a decomposition reaction occurs from the 3.2V neighborhood at the time of charge, and a lot of lithium ions deactivate.
[0010] This invention was made in view of this conventional trouble, and tends to offer the rechargeable lithium-ion battery which can demonstrate the charge-and-discharge property which was excellent when the lithium manganic acid ghost which has Spinel structure was used for a positive electrode.
[0011]
[Means for Solving the Problem] In the rechargeable lithium-ion battery which consists of the positive electrode containing the lithium manganic acid ghost to which invention according to claim 1 has Spinel structure, a negative electrode containing a carbon material, and the organic electrolytic solution, the above-mentioned organic electrolytic solution is in the rechargeable lithium-ion battery characterized by containing malonic-acid diester 0.5 to 3.0% by the volume.
[0012] What should be most observed in this invention is using the electrolytic solution which is carrying out [above-mentioned] the amount content of specification of the above-mentioned malonic-acid diester as the above-mentioned organic electrolytic solution. The above-mentioned organic electrolytic solution consists of a solvent and a supporting electrolyte. This invention makes this contain 0.5 - 3.0% of malonic-acid diester by the volume, when this whole solvent is made into 100%.
[0013] When the content of malonic-acid diester is less than 0.5%, there is a problem that there is little improvement effectiveness of the cycle property of a rechargeable lithium-ion battery. On the other hand, in exceeding 3.0%, disassembly of the solvent at the time of charge becomes large, and there is a problem that a cycle property deteriorates on the contrary.
[0014] As an example of malonic-acid diester, there are dimethyl malonate, a diethyl malonate, di-n-propylmalonate, ********** iso-propyl, di-n-butyl malonate, malonic-acid dibenzyl, etc. These malonic-acid diester may be used by the one-kind independent, and may be used two or more sorts if needed. As for the above-mentioned malonic-acid diester, like especially invention according to claim 2, it is desirable that they are a diethyl malonate or di-n-propylmalonate. Especially these are effective in improvement in the above-mentioned cycle property.
[0015] Mixed solvents, such as a solvent which for example already contains sulfur, such as lactone, such as chain-like carbonate, such as annular carbonate, such as well-known ethylene carbonate and propylene carbonate, dimethyl carbonate, diethyl carbonate, and ethyl carbonate methyl, gamma-butyrolactone, gamma-hexano lactone, a valerolactone, and epsilon-caprolactone, a sulfolane, a butane ape ton, and a propane ape ton, can be used for 97 - 99.5% of solvents other than malonic-acid diester. As a supporting electrolyte of the electrolytic solution, there are LiPF6, LiBF4, LiClO4, LiAsF6, LiN (CF3SO2)2, etc., for example.
[0016] Moreover, as a lithium manganic acid ghost of the above-mentioned positive electrode, well-known various things, for example, a lithium manganese spinel, a lithium manganese spinel with a superfluous lithium, the lithium manganese spinels that permuted a part of Mn with dissimilar metals, such as nickel, aluminum, Co, Fe, and Mg, those mixture, etc. can be used. A well-known natural graphite, an artificial graphite, corks, and the carbon that calcinated raw coke can be used for the carbon material of the above-mentioned negative electrode, for example.
[0017] Next, it explains per operation of this invention. The rechargeable lithium-ion battery of this invention contains the malonic-acid diester of the above-mentioned amount of specification as the above-mentioned organic electrolytic solution. Therefore, also when the above-mentioned lithium manganic acid ghost is used for a positive electrode, a cycle property improves greatly conventionally.
[0018] Although the reason of this improvement in a cycle property is not certain, it is thought that it is in building the good coat which malonic-acid diester decomposes on a negative-electrode front face at the time of charge, and makes receipts and payments of a lithium ion prompt at it. Hereafter, this operation effectiveness is explained in full detail using the example of an operation gestalt.
[0019]
[Embodiment of the Invention] It explains using one example E1 and one example C1 of a comparison about the rechargeable lithium-ion battery concerning the example of an operation gestalt of example of operation gestalt 1 this invention. The rechargeable lithium-ion battery concerning an example E1 consists of the positive electrode containing the lithium manganic acid ghost which has Spinel structure, a negative electrode containing a carbon material, and the organic electrolytic solution, and the above-mentioned organic electrolytic solution contains malonic-acid diester 0.5 to 3.0% by the volume. Hereafter, it explains first per manufacture approach of this example E1 and the example C1 of a

comparison.
[0020] (Example E1) First, 7 weight sections were mixed [lithium manganese spinel Li1.03Mn 1.97O4 (made in Honjo Chemical) / carbon black TB 5500 (Tokai Carbon make) / sections / 7 / weight] with N-methyl pyrrolidone NMP for polyvinylidene fluoride PVDF (product made from the Kureha chemistry) with 90 weight sections, and the slurry was prepared. Subsequently, the positive electrode whose thickness of electrode material is 53 micrometers was obtained by carrying out coating of the slurry, pressurizing it on an aluminum book, drying after that and piercing in a disk with a diameter of 15mm.
[0021] Next, 5 weight sections were mixed [the spherical artificial graphite MCMB2528 (Osaka Gas chemical **)] with NMP for 95 weight sections and above PVDF, and the slurry was prepared. Coating of the slurry was carried out to copper foil, and it was pressurized, and after that, it dried, pierced in the disk with a diameter of 17mm, and the negative electrode whose thickness of electrode material is 40 micrometers was obtained.
[0022] Next, 1 mol/L The organic electrolytic solution which added the di-n-propylmalonate (Tokyo formation make) as malonic-acid diester to LiBF4/EC+DEC (a mixing ratio 1:1, EC: volume of a solvent ethylene carbonate, DEC; diethyl carbonate) (product made from the Toyama pharmaceutical industry) 1% by the volume was produced. And the coin cell of cell capacity abbreviation 2mAh was produced using this organic electrolytic solution, the above-mentioned positive electrode and a negative electrode, and the Tonen Chemical polyethylene separator.
[0023] (Example C1 of a comparison) The rechargeable lithium-ion battery of this example of a comparison was produced like the example E1 except having used the electrolytic solution which does not contain malonic-acid diester instead of the organic electrolytic solution in an example E1.
[0024] Next, in this example, the cycle property of the coin cell (rechargeable lithium-ion battery) concerning an example E1 and the example E1 of a comparison was measured. Charge conditions put each coin cell on a condition with a temperature of 25 degrees C, and charge it to 4.2V by the constant current of current density 1.0 mA/cm2, a pan is charged by the constant voltage of 4.2V, and it was made for these charging times to turn into a total of 4 hours. Moreover, discharge conditions were made into the conditions of discharging to 3.0V by the constant current of current density 0.5 mA/cm2 after stopping for 10 minutes after the completion of charge. And this charge and discharge were repeated and the cycle property was measured.
[0025] The cycle property of each coin cell is shown in drawing 1 . This drawing takes the number of cycles along an axis of abscissa, and takes the discharge capacity (mAh/g) per positive active material along an axis of ordinate. As known in this drawing, the example E1 which makes the organic electrolytic solution come to contain malonic-acid diester (di-n-propylmalonate) has a discharge capacity higher than the comparison article C1 which does not contain malonic-acid diester over the whole measurement region, and it turns out that it excels in the cycle property.
[0026] The example of two examples of an operation gestalt is an example which investigated the effect by the content of the malonic-acid diester in the organic electrolytic solution, and the effect by adding an additive which replaces with malonic-acid diester and is different to the organic electrolytic solution. As a sample, four examples (E2-E4) as this invention article and seven examples of a comparison as a comparison article (C2-C8) were prepared. Below, these manufacture approaches are shown first.
[0027] (Example E2) The artificial graphite (Lonza make) was used for lithium manganese spinel Li1.10Mn 1.90O4 (made in Honjo Chemical) with 86 weight sections, 4 weight sections were used for PVDF (product made from the Kureha chemistry) with 10 weight sections, and the positive electrode whose thickness of the diameter of 15mm and electrode material is 52 micrometers was produced.
[0028] Next, after making a carboxymethyl-cellulose water solution suspend natural-graphite LF20A (product made from a China-Vietnam graphite), the negative-electrode active material which covered the front face of a natural graphite by amorphous carbon material was obtained by filtering and heating at the temperature of 700 degrees C under argon atmosphere. Next, after having mixed [this negative-electrode active material] the 7.5 weight sections with NMP for PVDF with the 92.5 weight sections, building the slurry and carrying out coating to copper foil, it pierced to discoid with a diameter of 17mm, and the negative electrode was obtained.
[0029] Next, 1mol/L The organic electrolytic solution which added the diethyl malonate as malonic-acid diester to LiPF6/EC+DEC (volume mixing ratio 3:7) (product made from the Toyama pharmaceutical industry) 0.5% by the volume was produced. And the coin cell was produced using this organic electrolytic solution, the above-mentioned positive electrode and a negative electrode, and the Tonen Chemical polyethylene separator.
[0030] (Example E3) Except that the amount of a diethyl malonate is 1.0%, it is the same as an example E2.
(Example E4) Except that the amount of a diethyl malonate is 2.0%, it is the same as an example E2.
(Example E5) Except that the amount of a diethyl malonate is 3.0%, it is the same as an example E2.
[0031] (Example C2 of a comparison) Except that the amount of a diethyl malonate is 0%, it is the same as an example

E2.
(Example C3 of a comparison) Except that the amount of a diethyl malonate is 0.2%, it is the same as an example E2.
(Example C4 of a comparison) Except that the amount of a diethyl malonate is 5%, it is the same as an example E2.
(Example C5 of a comparison) Except that the amount of a diethyl malonate is 15%, it is the same as an example E2.
[0032] (Example C6 of a comparison) It is the same as an example E2 except having used methyl benzoate 0.5% instead of the diethyl malonate.
(Example C7 of a comparison) as the solvent of the organic electrolytic solution -- the volume of EC, DEC, and methyl benzoate -- it is the same as an example E2 except having used the mixed solvent of a mixing ratio 1:1:1. Here, the above-mentioned examples C6 and C7 of a comparison are shown in JP,10-255836,A, and apply ** to a manganese system cell.
(Example C8 of a comparison) It is the same as an example E2 except having used n-butyl lactate 1.0% instead of the diethyl malonate.
[0033] Next, the cycle property of the coin cell concerning each example and the example of a comparison was measured. About charge-and-discharge conditions, it was presupposed that it is the same as that of the example 1 of an operation gestalt. A measurement result is shown in Table 1. 1 cycle eye and 10 cycle eye were shown in Table 1 as a discharge capacity per positive active material.
[0034]
[Table 1]
(表1)

試料	マロン酸ジエステル含有量(%)	正極活物質当たりの放電容量(mAh／g)	
		1サイクル目	10サイクル目
比較例C2	0.0	80.4	41.2
比較例C3	0.2	80.6	42.2
実施例E2	0.5	81.4	53.8
実施例E3	1.0	82.3	57.5
実施例E4	2.0	85.1	47.1
実施例E5	3.0	83.3	44.5
比較例C4	5.0	67.5	37.4
比較例C5	15.0	37.6	25.1
比較例C6	0.5(安息香酸メチル)	78.4	32.4
比較例C7	33.3(安息香酸メチル)	10.3	0.8
比較例C8	1.0(乳酸n-ブチル)	69.5	13.4
実施例E6	1.0	105.4	78.9
比較例C9	0.0	104.6	74.5

[0035] As known in Table 1, all, compared with the examples C2-C5 of a comparison, 1 cycle eye and 10 cycle eye also had a high discharge capacity, and the examples E2-E5 which are this invention articles showed the outstanding cycle property. From this result, the content of malonic-acid diester is understood that it is most desirable that it is 0.5 - 3.0% by the volume. Moreover, the examples C6-C8 of a comparison show that there is almost no effectiveness in improvement in a cycle property, when benzoin methyl or n-butyl lactate is added to the solvent of the organic electrolytic solution. It turns out that it is very effective to make the organic electrolytic solution contain malonic-acid diester like examples E2-E5 also from this.
[0036] The example of three examples of an operation gestalt is an example at the time of using the positive active material in each above-mentioned rechargeable lithium-ion battery, and different positive active material. And the example E6 was prepared as this invention article, and the example C9 of a comparison was prepared as a comparison article.
[0037] (Example E6) Lithium manganese spinel Li1.05aluminum0.05Mn 1.90O4 which permuted a part of Mn of the positive active material in an example E1 with aluminum was used for the coin cell (rechargeable lithium-ion battery) of this example as positive active material. Moreover, using a lithium carbonate, 4 oxidation 3 manganese, and an aluminium nitrate, in atmospheric air with a temperature of 900 degrees C, this positive active material was heated for 10 hours, and was obtained. It is the same as an example E1 except this positive active material. Therefore, in the

organic electrolytic solution of this example, the di-n-propylmalonate as malonic-acid diester is contained 1% by the volume.

[0038] (Example C9 of a comparison) It is the same as an example E6 except the percentage of di-n-propylmalonate being 0%.

[0039] Next, the cycle property of the coin cell concerning an example E6 and the example C9 of a comparison was measured. About charge-and-discharge conditions, it was presupposed that it is the same as that of the example 1 of an operation gestalt. A measurement result is collectively shown in the above-mentioned table 1. 1 cycle eye and 10 cycle eye were shown in Table 1 as a discharge capacity per positive active material.

[0040] As known in Table 1, compared with the example C9 of a comparison, 1 cycle eye and 10 cycle eye also had a high discharge capacity, and the example E6 showed the outstanding cycle property. This also shows that it is effective in the improvement in a cycle property of a rechargeable lithium-ion battery to make the organic electrolytic solution contain malonic-acid diester. In addition, the level of the discharge capacity of an example E6 and the example C9 of a comparison is because, as for high one, positive active material differs compared with the above-mentioned examples E1-E5 and the examples C1-C8 of a comparison.

[0041]

[Effect of the Invention] According to this invention, like ****, the rechargeable lithium-ion battery which can demonstrate the charge-and-discharge property which was excellent when the lithium manganic acid ghost which has Spinel structure was used for a positive electrode can be offered.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] It is the rechargeable lithium-ion battery characterized by the above-mentioned organic electrolytic solution containing malonic-acid diester 0.5 to 3.0% by the volume in the rechargeable lithium-ion battery which consists of the positive electrode containing the lithium manganic acid ghost which has Spinel structure, a negative electrode containing a carbon material, and the organic electrolytic solution.
[Claim 2] It is the rechargeable lithium-ion battery characterized by the above-mentioned malonic-acid diester being a diethyl malonate or di-n-propylmalonate in claim 1.

[Translation done.]